

STUDYING THE OPTICAL CHARACTERISTICS OF POLY-METHYL METHACRYLATE PMMA FILMS DOPED WITH FLUORESCEINEOSIN-Y DYE

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ABSTRACT

In this paper, films of pure poly-methyl methacrylate PMMA and doped with Eosin-Y dye with (0.1 mm) thickness were prepared by solution casting technique. A (1 gm) of PMMA polymer in the shape of grain were solved in (100 ml) of chloroform. Eosin-Y dye added to the polymer in different concentration (10^{-4} , 10^{-5} , 10^{-6} mol/L). The optical properties (Absorbance, Transmittance, Reflectance) of the pure and doped films were studied by using the spectrometer in the range (200-800 nm). The optical constants: Absorption Coefficient, Refractive Index (n), Energy Gap (Eg), Extinction Coefficient (k), for pure of polymethyl methacrylate PMMA and doped by Eosin-Y dye were calculated. These studies have done to show the effect of adding the Eosin-Y dye on the optical properties of pure PMMA. The results show shifting to the visible area for the optical properties and decreasing in the optical constants after adding the dye.

KEYWORDS: PMMA Polymer, Eosin-Y Dye, Optical Constants, Optical Properties & Energy Gap

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1. INTRODUCTION

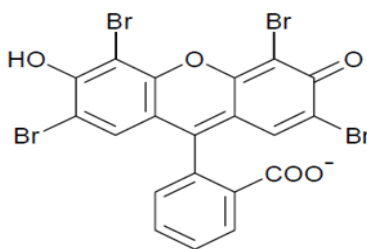
Polymers are important material because they are regarded as a cheap, alternative material, and easy manufacturing. Polymers are used widely in various fields such as optical communications, industrial products, optical waveguides and optical connector [1]. Polymethyl methacrylate (PMMA) has special interest due to its physical and optical properties.

The properties of PMMA showed by literature studies depend on the molecular structure. These properties can be modified by several methods like UV illumination, polymer blending, and external electric field. [2]

There are several dyes with name Eosin. Eosin Y is a pink acid dye soluble in water which also displays yellow-green fluorescence. It has a molecular formula of $C_{20}H_8Br_4O_5$ and a molecular weight of 647.89. [3]. Eosin Y has a shoulder at 475 nm and a maximum at 510 nm. [4]

Eosin Y is a synthetic dye and used in many applications. Its molecular formula is $C_{20}H_8Br_4O_5$ and a molecular weight equal 647.89. It is a pink water-soluble acid dye. It was reported that eosin Y shows yellow-green fluorescence [5].

Eosin Y is a dye which is a water soluble acid also displays yellow-green fluorescence (Scheme I).



Scheme I: Chemical Structure of Eosin - Y [6]

2. THEORETICAL PART

There is a relation between incident intensity (I) and the penetrating light intensity (I_0) expressed by the relation: [7]

$$I = I_0 e^{-\alpha t} \quad (1)$$

t - the thickness of material samples in (cm)

α - the absorption coefficient in (cm^{-1})

The absorption coefficient calculated by the equation:[8]

$$\alpha = 2.303 (A / t) \quad (2)$$

Where (A) represents the absorbance.

For specific thickness, the absorption coefficient written as:[9]

$$\alpha_t = 2.303 \log (I/I_0) \quad (3)$$

Absorbance (A) represented by the mount of $\log (I/I_0)$.

The value of absorption coefficient determines if the electronic transition were direct or not where if $\alpha \geq 10^4 \text{ cm}^{-1}$ that mean the electronic transition is direct.[2]

The optical energy gap may be evaluated by the relation:[10]

$$\alpha h\nu = A(h\nu - E_g)^m \quad (4)$$

The ($h\nu$) represent the photon energy, (A) represents the proportional constant, (m) represent constant, (E_g) present the forbidden or allowed energy gap.

The reflectance may be calculated by using the values of absorbance and transmittance by the following Equation:[11]

$$R = 1 - A = 1 - T = 1 \quad (5)$$

R = reflectivity, k = extinction coefficient, and n = refractive index.

The equation of extinction coefficient can be written as:[12]

$$K = \alpha \lambda / 4\pi \quad (6)$$

λ = the wavelength of incident rays.

3. EXPERIMENTAL PART

The Polymethyl methacrylate (pmma) polymer films doped with Eosin Y dye were prepared in the laboratory by solution casting technique. The concentrations of dye were (10^{-4} , 10^{-5} , 10^{-6})wt%.

The desired concentrations of the prepared dye were calculated by the equation:[13]

$$W = MW \times V \times C / 1000 \quad (7)$$

Where W = dissolved dye weight

M_w = dye molecular weight

C = the concentration of dye

In glass beaker, (100) ml of chloroform added to dissolve (1) gm of PMMA polymer by using magnetic stirrer and the final solvent put in Petri dish (5 cm) diameter cleaned with alcohol. The dishes left in laboratory covered with white paper for 3 days to complete the evaporation of the solvent, the thickness of samples were (0.01 mm) measured by digital micrometer calculated by taking the average value of many directions measurements.

The optical measurements made by using Mega-2100 Double Beam UV-VIS Spectrophotometer in the range (200-800 nm) while the fluorescent measurements made by F96 pro fluorescence spectrophotometer to investigate the effect of adding fluorescent dye in deferent concentrations to the polymer.

4. RESULTS AND DISCUSSIONS

The absorption and transmission spectrum recorded in the range (200-800 nm) studied for pure and doped samples as shown in figure (1 and 2). From the figures, we can observe the decreasing in the absorbance and transmittance with decreasing concentrations of added Eosin Y dye. Before adding the dye, polymer PMMA has high absorbance and a low transmittance in the UV region about 322 nm. Fundamental absorption edge shifted to lower energies and longer wavelengths after addition as indicated which mean there is a chemical interaction between the polymer and the dye.

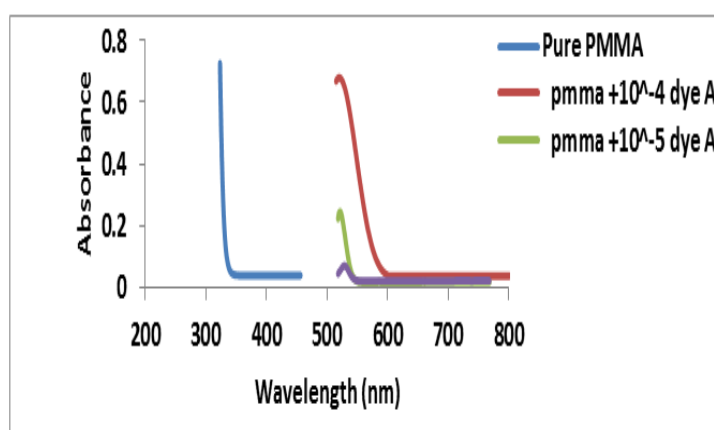


Figure 1: Absorption Spectrum for Pure and Doped Films

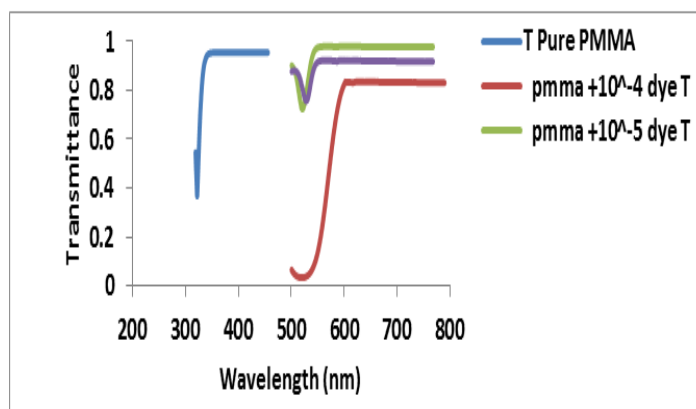


Figure 2: Transmission Spectrum for Pure and Doped Films

Reflectance for pure and doped samples calculated by using the equation (5). Figure (3) represents the reflectance for pure and doped samples. The reflectance decreased with decreasing dye concentrations because of absorbing of electromagnetic energy of incident light by outer electrons and shifted to longer wavelengths. At energies less than the energy of the bandgap the reflectance increase rapidly. Increasing in the values of reflectance with increasing the energy of photons until reach maximum values mean that photon energy corresponding the energy gap.

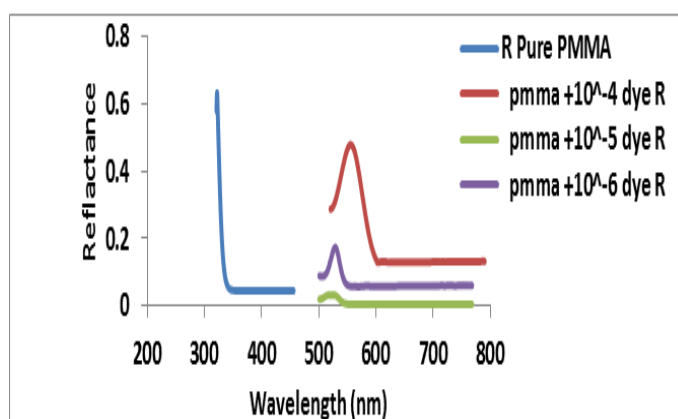


Figure 3: Reflection Spectrum for Pure and Doped Films

The optical constants, Extinction Coefficient (k), Absorption Coefficient, Energy Gap (E_g), for pure samples were calculated by using the equations declare in the theoretical part as shown in figures (4,5,6 and 7).

Extinction Coefficient (K) explain the absorption of energy when the electromagnetic wave travels in the material. The extinction coefficient values depend on free electrons density. Figure (4) clear the relation of K vs photon energy for pure and doped samples one can notice a small value of k for pure sample and this value increase by increasing the concentration of dye.

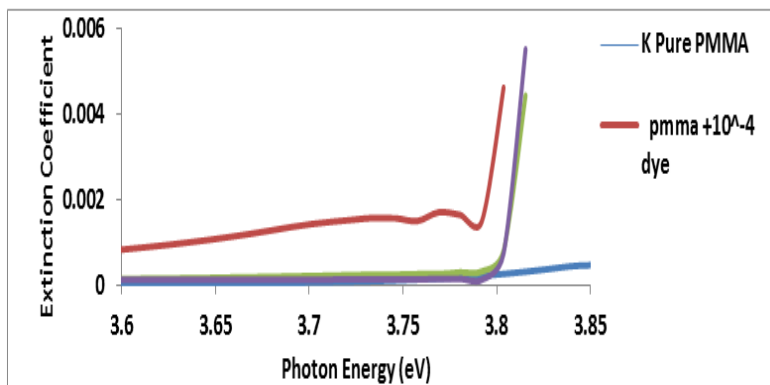


Figure 4: Extinction Coefficient as a Function of Wavelength for Pure and Doped Samples

There is a relation between the extinction coefficient and absorption coefficient determined by the equation (6). The absorption coefficient behaves just like the extinction coefficient as clear in figure (5) where the absorption coefficient increase after adding the dye and increases by increasing concentrations of dye. From figure (5) we can see the absorption coefficient is small for small energies which mean that the incident photon energy is not equal to the difference of the energy between the valance and conduction bands ($E_{ph} < E_g$).

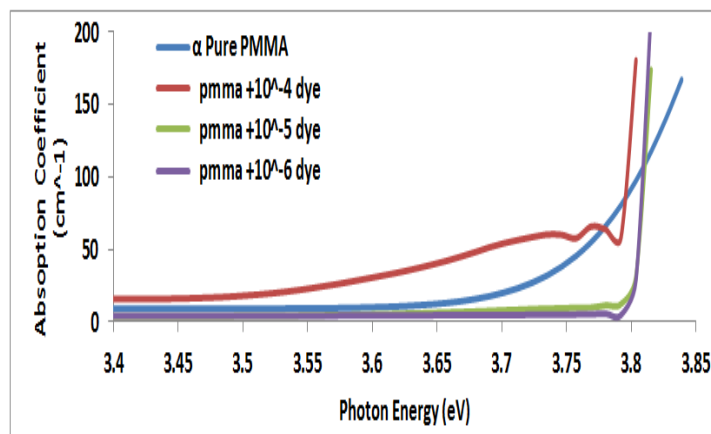


Figure 5: Absorption Coefficient as a Function of Photon Energy for Pure and Doped Films

Drawing the relation between $(\alpha h\nu)^2$ and photon energy gives the values of energy gaps for pure and doped samples in different concentration. Figure (6) is plotted for pure sample and the energy gap found to be equal (3.8 eV). Figures (7,8 and 9) plotted for doped samples. The values of energy gap according to adding (1×10^{-4} , 1×10^{-5} , and 1×10^{-6} mol/L) equal to (2.14, 2.26, and 2.22 eV) respectively. Noticing the figures before and after doping one can found decreasing in the value of energy gap because of adding Eosin Y dye. These decreasing came from creation of level sites in the forbidden energy gap. These sites of levels make the energy gap narrower so the electrons cross the energy gap with less photon energy.

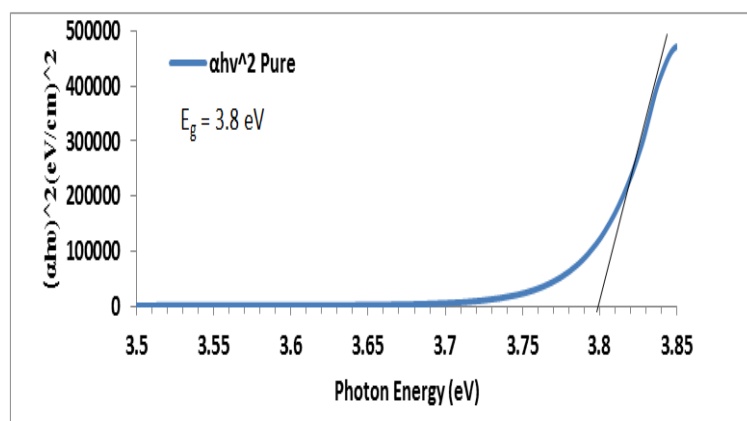


Figure 6: $(\alpha h\nu)^2$ as Function of Photon Energy for Pure Sample

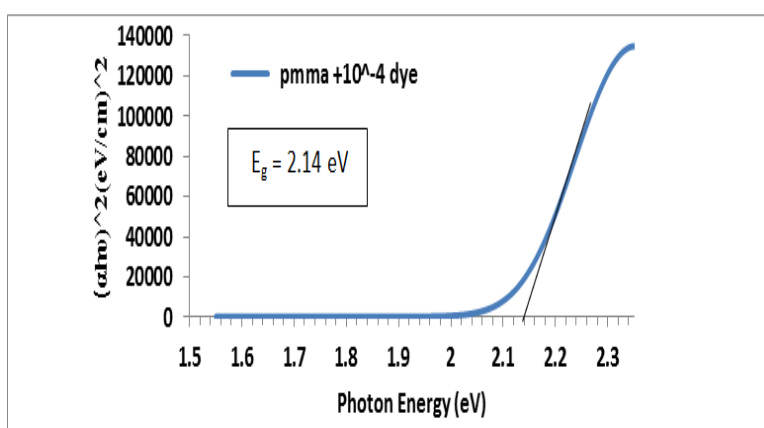


Figure 7: $(\alpha h\nu)^2$ as Function of Photon Energy for PMMA Doped with 1×10^{-4} Eosin Dye

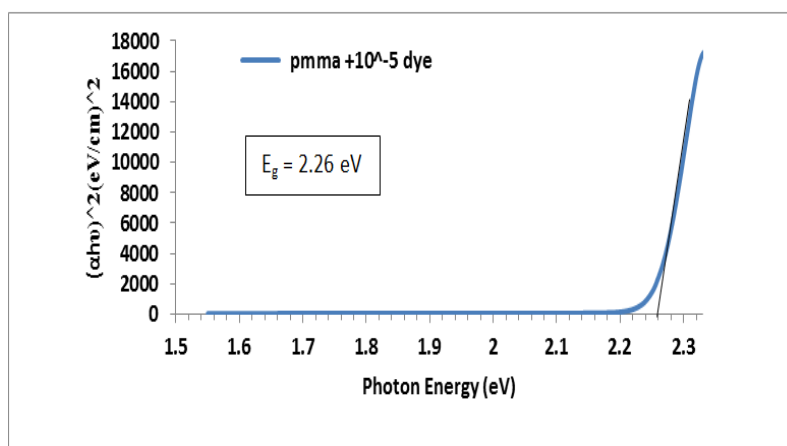


Figure 8: $(\alpha h\nu)^2$ as Function of Photon Energy for PMMA Doped with 1×10^{-5} Eosin Dye

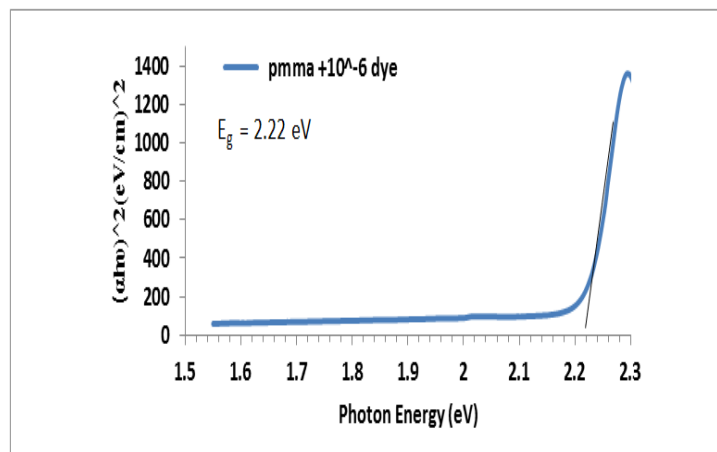


Figure 9: $(\alpha h\nu)^2$ as Function of Photon Energy for PMMA Doped with 1×10^{-6} Eosin Dye

The fluorescent spectrum as a function of wavelength recorded by F96 pro Fluorescence spectrophotometer for different concentration of Eosin Y dye before and after addition to solvent PMMA polymer. The results recorded by the spectrophotometer justify by figures (10, 11, and 12) for (1×10^{-4} , 1×10^{-5} , and 1×10^{-6} mol/L) respectively. It is clear from the figures the effect of adding fluorescent dye to the polymer by shifting the peak of intensity to longer wavelength for all prepared samples.

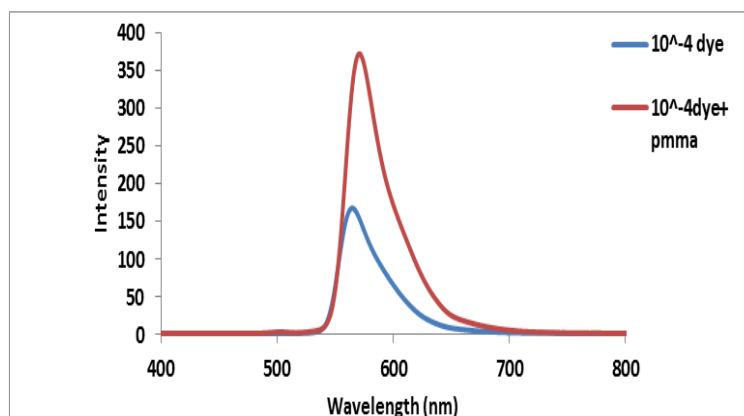


Figure 10: Fluorescent Spectrum Vs Wavelength for 1×10^{-4} Eosin and PMMA + 1×10^{-4} Eosin

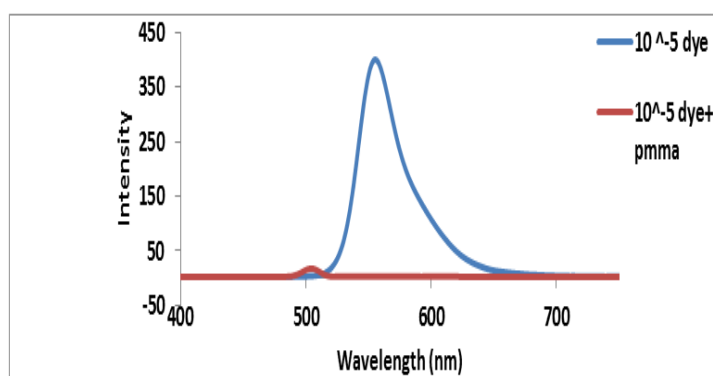
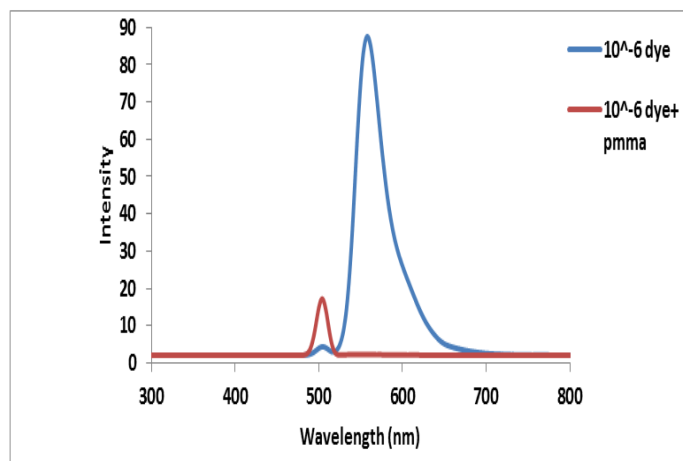


Figure 11: Fluorescent Spectrum Vs Wavelength for 1×10^{-5} Eosin and PMMA + 1×10^{-5} Eosin



**Figure (12) Fluorescent Spectrum Vs Wavelength
for 1×10^{-6} Eosin and PMMA + 1×10^{-6} Eosin**

5. CONCLUSIONS

All the optical properties and optical constants of PMMA polymer effected by adding Eosin Y fluorescent dye in different concentrations.

- Absorbance, transmittance, and reflectance decrease because of adding Eosin Y fluorescent dye but there were shifting to the longer wavelengths.
- Increasing in the extinction coefficient and the absorption coefficient after adding Eosin Y fluorescent dye in different concentrations.
- Decreasing in the value of the energy gap after adding Eosin Y dye because of sits level formed in the energy gab after adding Eosin Y fluorescent dye in different concentrations.
- The fluorescent spectrum for pure samples affected by adding Eosin Y fluorescent dye in different concentrations and shifted to the longer wavelengths.

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